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**EPA Agreement Number:** R82806001-0

**Title:** PM<sub>2.5</sub> Technology Assessment and Characterization Study in New York State (PMTACS-NY)

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**Institution:** Atmospheric Sciences Research Center, University at Albany

**Cost Sharing Partners:** New York State Energy Research and Development Authority (NYSERDA) and New York State Department of Environmental Conservation (NYSDEC)

**Research Category:** Particulate Matter EPA "Supersites" Program

**Sorting Code:** 99-NCERQA-X1

**Project Period:** October – December 2002

### **Objective of Research:**

As a result of recent clinical and epidemiological studies (NRC, 1998) associating adverse health effects in humans and fine particle mass, a new National Ambient Air Quality Standard for PM<sub>2.5</sub> mass (15 µg/m<sup>3</sup> annual and 65 µg/m<sup>3</sup> 24-hr average) has been promulgated in the United States (Federal Register, 1997). Significant scientific and technical issues surrounding the mitigation of the warm season PM<sub>2.5</sub> /co-pollutant complex and its interdependence with O<sub>3</sub> air quality through coupled photochemical pathways, common precursors, and similar dependencies upon meteorology must be addressed if effective control strategies are to be implemented.

The long-term monitoring of the PM<sub>2.5</sub>/co-pollutant complex and its precursors at urban and regional representative sites provides the opportunity to track the impact of emission controls and their effectiveness on air quality. These data can be used to verify that implemented PM<sub>2.5</sub> primary and secondary precursor (including ozone precursor) emission controls are performing according to specifications and verify that PM<sub>2.5</sub> and ozone air quality has responded to the emission changes achieved as expected. Without adequate monitoring systems to track the progress and effectiveness of implemented control programs, the air quality management approach remains unaccountable.

The PMTACS-NY Supersite program provides a unique and unparalleled opportunity to enhance our understanding of ozone/PM<sub>2.5</sub>-precursor relationships and track progress in current precursor emission control programs and assess their effectiveness in achieving expected air quality responses. The impact of this research is highly significant, providing a sound scientific basis for informed effective decisions in the management of air quality in New York and will benefit its citizens both environmentally and economically.

The PMTACS-NY is designed around three major objectives and addresses a series of science policy relevant questions related to hypotheses to be tested using measurement data collected under the program. The subject quarterly reports provide highlights on the overall program status, the progress made in the context of the specific tasks associated with the three program objectives, identification of outstanding issues, project schedule and completion status by task, and a budget analysis.

### **Progress Summary/Accomplishments:**

The reduction of the measurement data from summer mini-intensive at Whiteface Mountain has begun with the goal to have a data review workshop/meeting in February of 2003. During this quarter our research team worked on the preparation and participation in several scientific conferences presenting results and findings from our Supersite 2001 Summer Intensive in Queens, NY and in the organization and preparation for a January 2003 PI's Supersite meeting in Atlanta, GA (see publication/presentation section of this report).

**Objective I.** Measure the temporal and spatial distribution of the PM<sub>2.5</sub>/co-Pollutant complex including: SO<sub>2</sub>, CO, VOCs/Air Toxics, NO, NO<sub>2</sub>, O<sub>3</sub>, NO<sub>y</sub>, H<sub>2</sub>CO, HNO<sub>3</sub>, HONO, PM<sub>2.5</sub> (mass, SO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, OC, EC, Trace Elements), single particle aerosol composition, CN, OH and HO<sub>2</sub> to support regulatory requirements to develop cost effective mitigation strategies PM<sub>2.5</sub> and its co-pollutants and to establish trends in the relevant precursor concentrations to assess the impact of recent and future emission reductions in terms of emission control effectiveness and air quality response.

Measurements at our two rural sites Whiteface Mountain and Pinnacle State Park operated during the quarter as outlined in Table 1 of the QAPP, with the obvious exception of the summer intensive period at Whiteface Mountain as outlined above. Our urban sites, IS 52 in the South Bronx and PS219 in Queens also operate monitoring equipment outline in Table 1 of the QAPP.

**Objective II.** Monitor the effectiveness of new emission control technologies [i.e. Compressed Natural Gas (CNG) bus deployment and Continuously Regenerating Technology (CRT)] introduced in New York City and its impact on ambient air quality, thorough remote open path roadside, mobile platform, and fixed site measurements of CO<sub>2</sub>, CO, NO, H<sub>2</sub>CO, HONO, CN and aerosol chemical composition.

Preparation of manuscript, entitled "Mobile Particulate Emission Studies of in-use New York City Vehicles", for submission to Aerosol Science and Technology reporting on results from vehicle chase studies is underway.

**Objective III.** Test and evaluate new measurement technologies and provide tech-transfer of demonstrated operationally robust technologies for network operation in support of the development of process science and observation based analysis tools and health based exposure assessments.

A summary of the testing, evaluation and intercomparison of semi-continuous PM sulfate and nitrate instrumentation operated during the Summer 2001 field intensive in Queens, NY presented in the poster session of the American Geophysical Union 2002 Fall Meeting, 6-10 December 2002, San Francisco, CA is provided at the end of this report.

**Publications/Presentations:**

Presentations at the 21<sup>st</sup> AAAR 2002 Annual Conference October 7-11, 2002 Charlotte, NC included:

<b>Presentation Title: Date - Platform – PL; Poster Session – PS</b>	<b>Lead Author:</b>
1. PMTACS-NY: An Overview of the 2001 Summer Intensive in Queens, NY-10/8 <b>PL 4A2</b>	Demerjian
2. Ongoing Development of a continuous reference standard PM mass monitor for ambient air... - 10/9 <b>PL AC1</b>	Patashnick
3. Intercomparison and Evaluation of four semi-continuous Particulate Sulfate Instruments ... - 10/9 <b>PL 5A1</b>	Drewnick
4. Intercomparison and Performance Evaluation of Semi-Continuous PM-2.5 Nitrate Instruments ...- 10/9 <b>PL 5A2</b>	Hogrefe
5. Measurement of Ambient Aerosol Composition using an Aerosol Mass Spectrometer: ...10/9 <b>PL 5D1</b>	Drewnick
6. Characterization of Continuous PM <sub>2.5</sub> Sulfate and Nitrate Instruments In an Aerosol Flow Chamber.10/10 <b>PL 10B1</b>	Rattigan
7. Regional Contributions to the Concentrations of Sulfate and Trace Elements in New York, New York. 10/11 / <b>PL 13A1</b>	Qureshi
8. Advances in Continuous Mass Measurement Technology: TEOM Mass Monitor at 30° C with a Nafion Dryer../ <b>PS PA3-04</b>	Schwab
9. Comparisons of Speciated PM-2.5 Mass at Rural and Urban New York State... / <b>PS PA3-07</b>	Felton
10. The ASRC Aerosol Generation, Calibration & Research Facility../ <b>PS P16-02</b>	Hogrefe

Presentations at the American Geophysical Union 2002 Fall Meeting, 6-10 December 2002, San Francisco, CA included: (Cite abstracts as *Eos Trans. AGU*, 83(47), Fall Meet. Suppl., Abstract xxxxx-xx, 2002).

<b>Poster Session A52C</b> SN: EPA PM Supersite Program: Results and Findings From the Summer 2001 Field Intensive Presiding Chair: K L Demerjian, University at Albany <b>Presentation Title:</b>	<b>Lead Author:</b>
<b>A52C-0128</b> <b>TI: PM2.5 Technology Assessment and Characterization Study in New York - PMTACS-NY: The 2001 Summer Field Intensive in Queens, NY</b> <b>A52C-0132</b> <b>TI: Intercomparison and Evaluation of Semi-Continuous PM-2.5 Nitrate and Sulfate Instruments During PMTACS-NY Summer 2001 Campaign in New York City</b> <b>A52C-0129</b> <b>TI: Measurement of Ambient Aerosol Composition Using an Aerosol Mass Spectrometer: New York 2001 Supersite Summer Intensive Study</b> <b>A52C-0126</b> <b>TI: Observations of OH, HO2 and OH Reactivity during PMTACS-NY2001: Comparison of Calculations and Observations</b> <b>A52C-0130</b> <b>TI: Mobile Particulate Emission Measurements of New York City Transit Buses and Other in use Vehicles</b> <b>A52C-0133</b> <b>TI: Comparisons of Speciated PM-2.5 Mass At Rural And Urban New York State Locations</b> <b>A52C-0131</b> <b>TI: Advances in Continuous Mass Measurement Technology: TEOM Mass Monitor at 30° C with a Nafion Dryer at Rural and Urban New York State Locations.</b>	Demerjian  Hogrefe  Drewnick  Ren, X  Jayne  Felton  Schwab

Presentation - **Environmental Quality Systems Symposium at Syracuse, October 29-30, 2002, Syracuse, NY** “PM2.5 Technology Assessment and Characterization Study in New York – PMTACS-NY: An Overview of the 2001 Summer Intensive in Queens, NY” Kenneth L. Demerjian

Presentation - **Air & Waste Management Association, Symposium on Air Quality Measurement Methods and Technology—2002 November 13-15, 2002 San Francisco, CA**  
 “Long-term Comparison of TEOM, SES TEOM, and FRM Measurements at Rural and Urban New York Sites”, James J. Schwab, John Spicer, Kenneth L. Demerjian, H. D. Felton, and Jeffrey Ambs.

The following three papers were submitted for publication in the “Supersites” Special Issue in Aerosol Science and Technology:

**Development and Operation of an Aerosol Generation, Calibration and Research Facility**  
 Olga Hogrefe, G. Garland Lala, James J. Schwab, Frank Drewnick and Kenneth L. Demerjian  
 Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY 12203.

**Measurement of Ambient Aerosol Composition during the PMTACS-NY 2001 using an Aerosol Mass Spectrometer - Part I: Mass Concentrations**  
 Frank Drewnick, James J. Schwab, John T. Jayne, Manjula Canagaratna, Douglas R. Worsnop, Kenneth L. Demerjian; Atmospheric Sciences Research Center, State University of New York, 251 Fuller Road,

Albany, NY 12203, USA (F.D., J.J.S., K.L.D.); Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc, 45 Manning Road, Billerica, MA 01821-3976 (J.T.J., M.C., D.R.W.).

**Measurement of Ambient Aerosol Composition during the PMTACS-NY 2001 using an Aerosol Mass Spectrometer - Part II: Chemically Speciated Mass Distributions**

Frank Drewnick, John T. Jayne, Manjula Canagaratna, Douglas R. Worsnop, Kenneth L. Demerjian; Atmospheric Sciences Research Center, State University of New York, 251 Fuller Road, Albany, NY 12203, USA (F.D., K.L.D.); Center for Aerosol and Cloud Chemistry, Aerodyne Research Inc, 45 Manning Road, Billerica, MA 01821-3976, USA (J.T.J., M.C., D.R.W.).

One paper has also been submitted to Atmospheric Environment:

**Intercomparison and Evaluation of Four Semi-continuous PM-2.5 Sulfate Instruments**

F. Drewnick, J. J. Schwab, O. Hogrefe, S. Peters, L. Husain<sup>1</sup>, D. Diamond<sup>2</sup>, R. Weber<sup>2</sup> and K. L. Demerjian; Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY

<sup>1</sup>NYS Department of Health, Wadsworth Center, Albany, NY

<sup>2</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA

**Future Activities and Outstanding Issues:** During the next quarter planned activities include:

1) convening a data workshop/meeting on the Whiteface Mountain Summer 2002 Field Intensive data set; 2) preparation and participation in the Supersite PIs meeting, January 22-23, 2003 in Atlanta, GA; 3) preparation for Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health AAAR Conference, March 31 – April 4, 2003, Pittsburgh, PA; and 4) preparation and submission of draft manuscripts for the 2<sup>nd</sup> Special Issues in Aerosol Science and Technology and 1<sup>st</sup> Special Issue in Atmospheric Environment.

Finally, in the original proposal we had intended to return to New York City to perform a counterpart field intensive (to that of the Summer 2001 program) in the winter of 2003 (i.e. January 15- February 15). We have decided to postpone this intensive until November 15 – December 15, 2003). This decision was based on several factors including delays in the construction of the NYS DEC's Queens College permanent monitoring facility, which is to host the intensive study. The current anticipated completion date for the site is late April – early May of 2003. In addition, the substantial demands on our researchers to perform data reduction, analysis and report of results/findings from the Queens College 2001 and Whiteface Mountain 2002 Summer intensives suggested that returning to the field on such a short lead time would be counter productive.

**Supplemental Keywords:** ambient air, atmospheric aerosols, ozone, particulate matter, metals, nitrogen oxides, sulfates, organics, atmospheric chemistry, monitoring, measurement methods, northeast air quality.

**Relevant Web Sites:** <http://www.asrc.cestm.albany.edu/pmtacsny/>



# Intercomparison and Evaluation of Semi-Continuous PM-2.5 Nitrate and Sulfate Instruments During PMTACS-NY Summer 2001 Campaign in New York City

Olga Hogrefe<sup>1</sup>, Frank Drewnick<sup>1</sup>, James J. Schwab<sup>1</sup>, H. D. Felton<sup>2</sup>, Kenneth L. Demerjian<sup>1</sup>

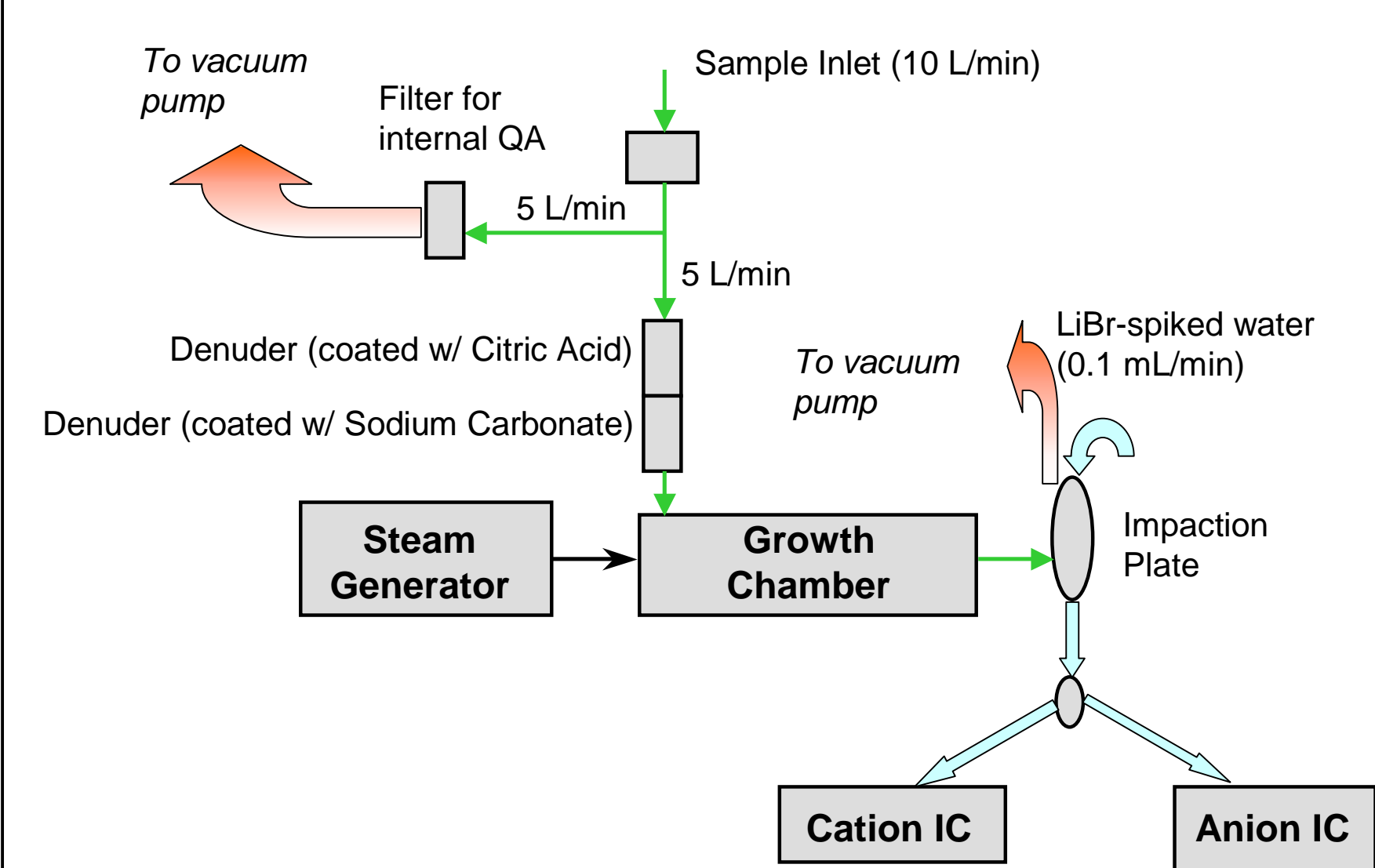
<sup>1</sup> - Atmospheric Sciences Research Center, U-Albany, State University of New York, 251 Fuller Rd, Albany, NY 12203; <sup>2</sup> - New York State Department of Environmental Conservation, Division of Air Resources, 625 Broadway, Albany, NY 12233



## Introduction

- PM2.5 Technology Assessment and Characterization Study** - New York (PMTACS-NY) is one of several U.S. EPA "Supersites" intended to provide enhanced measurement data on chemical and physical composition PM and its associated precursors.
- One of the PMTACS-NY objectives is evaluation of new measurement technologies and establishing their potential for routine monitoring.
- A variety of research-grade and commercial aerosol instruments were deployed and operated.
- Instruments used in this study: Particle-into-Liquid Sampler with Ion Chromatographs, Aerosol Mass Spectrometer, Ambient Particulate Nitrate and Sulfate Monitors and Continuous Ambient Sulfate Monitor.

## Design and Operation of Semi-Continuous Instruments



### Particle-into-Liquid Sampler with Ion Chromatographs (PILS-IC)

- R. Weber et. al, Georgia Tech
- Measures: SO<sub>4</sub>, NO<sub>3</sub>, NO<sub>2</sub>, other ionic species
- URG PM2.5 cyclone, denuders
- Turbulent mixing with saturated water vapor => particle growth
- Collection into a liquid flow
- Quantification of soluble components in ion chromatographs
- Cycle length: 15 min
- Sampling period: 7/1 – 8/5; Data completeness: 69%
- Minor operation problems only

### Aerosol Mass Spectrometer (AMS)

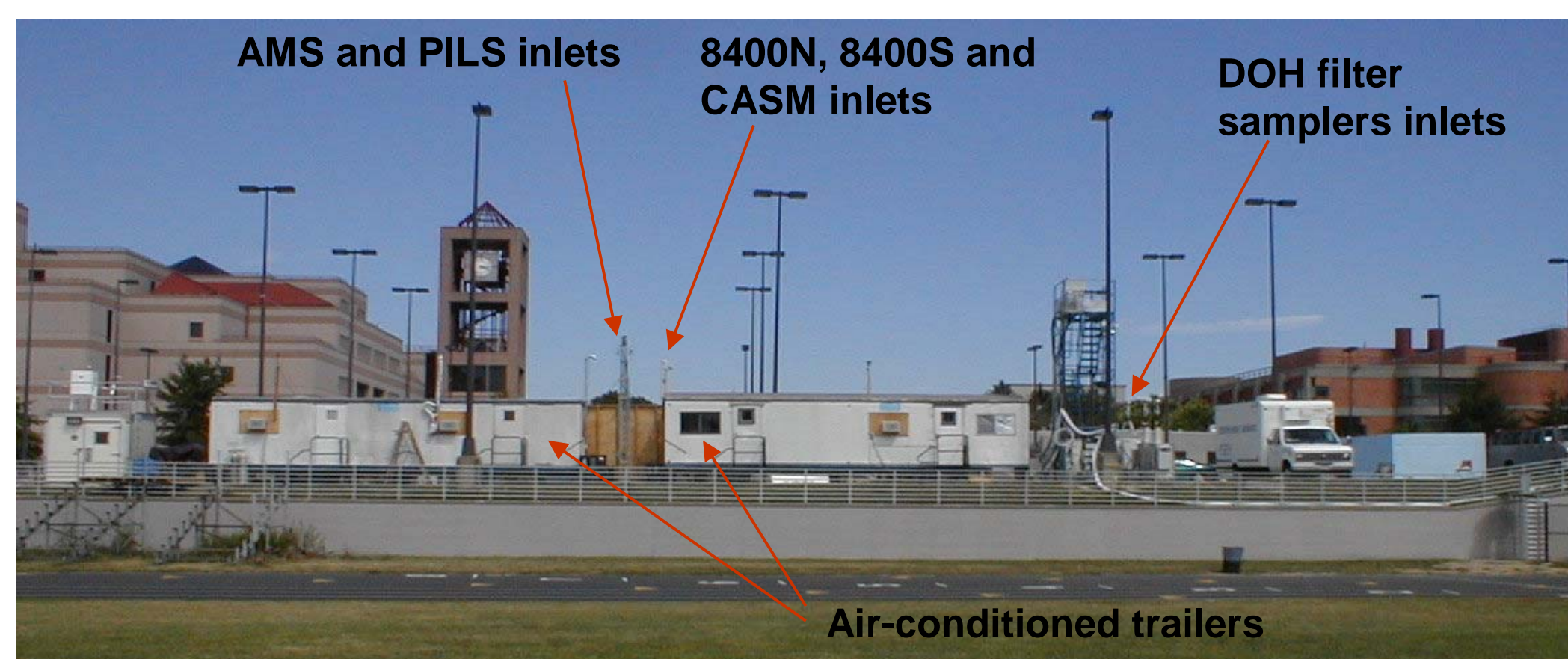
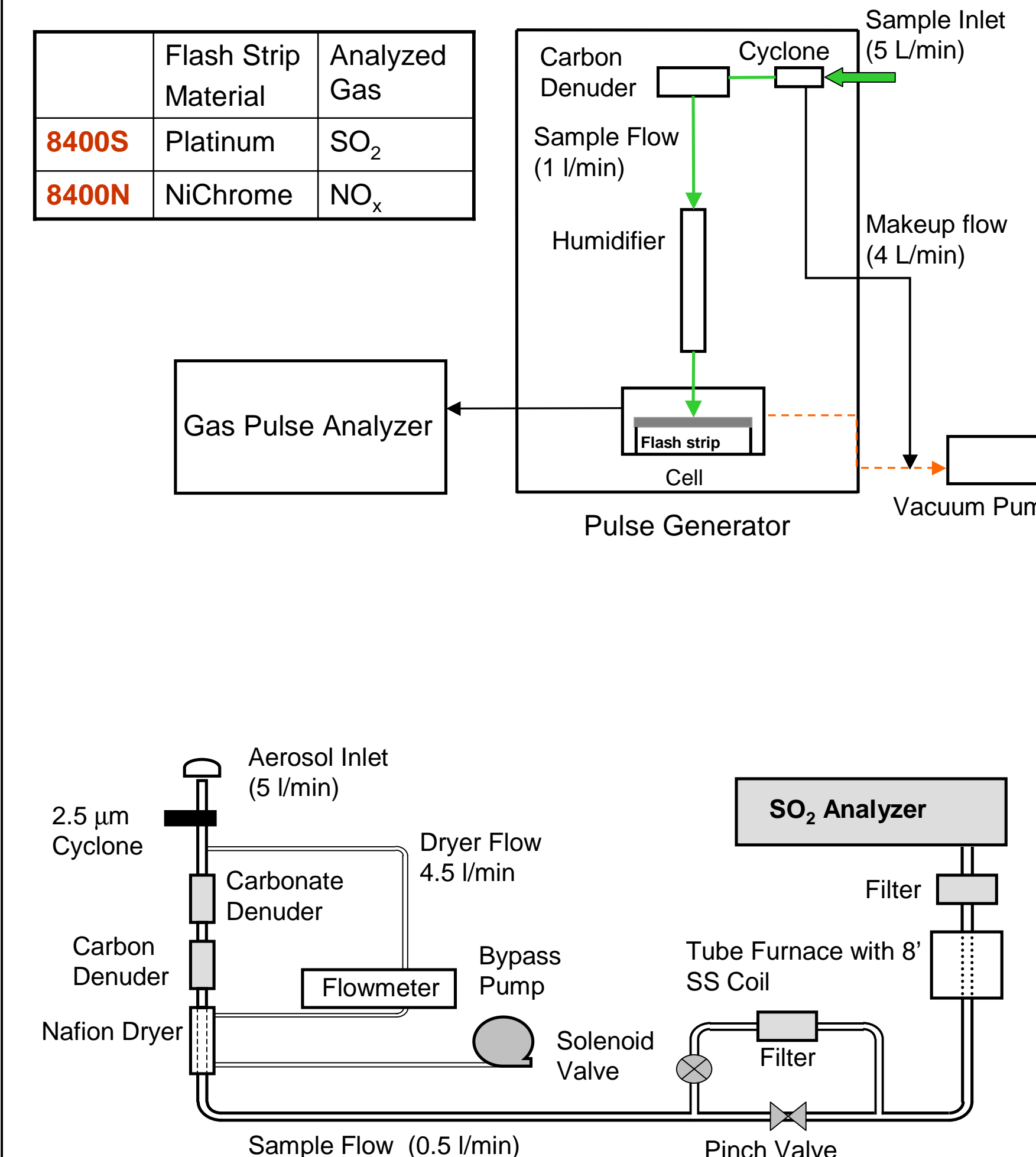
- Aerodyne Research Inc.
- Measures: SO<sub>4</sub>, NO<sub>3</sub>, other refractory species
- URG PM2.5 cyclone
- Focusing in aerodynamic lens
- Flash volatilization (700°C heater)
- Ionization by electron impact
- Alternating between "Mass Spec" and "Time of Flight" modes
- "Mass Spec" – bulk composition of aerosol
- "Time of Flight" – size distribution of aerosol components
- Averaging period: 10 min
- Sampling period: 6/30 – 8/5; Data completeness: 94%
- Major operation problem: random failures of data acquisition computer (has been solved)

### Ambient Particulate Sulfate and Nitrate Monitors (8400S and 8400N)

- Rupprecht and Patashnick Co., Inc.
- Measures: SO<sub>4</sub> (8400S), NO<sub>3</sub> (8400N)
- BGI SC PM2.5 cyclone
- Conditioning of air sample in humidifier
- Collection of aerosol on a metal strip
- Flash volatilization of aerosol
- Quantification of evolved oxides with gas analyzer
- Cycle length: 10 min
- Sampling period: 6/29 – 8/4 (8400N), 8/5 (8400S); Data completeness: 95% (8400S), 90% (8400N)
- Major operation problem: short lifetime of flashing strips (has been solved)

### Continuous Ambient Sulfate Monitor (CASM)

- G. Allen et al., Harvard School of Public Health, built in the field
- Measures: SO<sub>4</sub>
- BGI SC PM2.5 cyclone, denuders, dryer
- Evaporation and SO<sub>4</sub>-to-SO<sub>2</sub> conversion in stainless steel 900°C furnace
- Quantification of SO<sub>2</sub> with gas analyzer
- Sampling frequency: continuous, 1-hour aver.
- Sampling period: 7/22 – 8/5; Data completeness: 95%

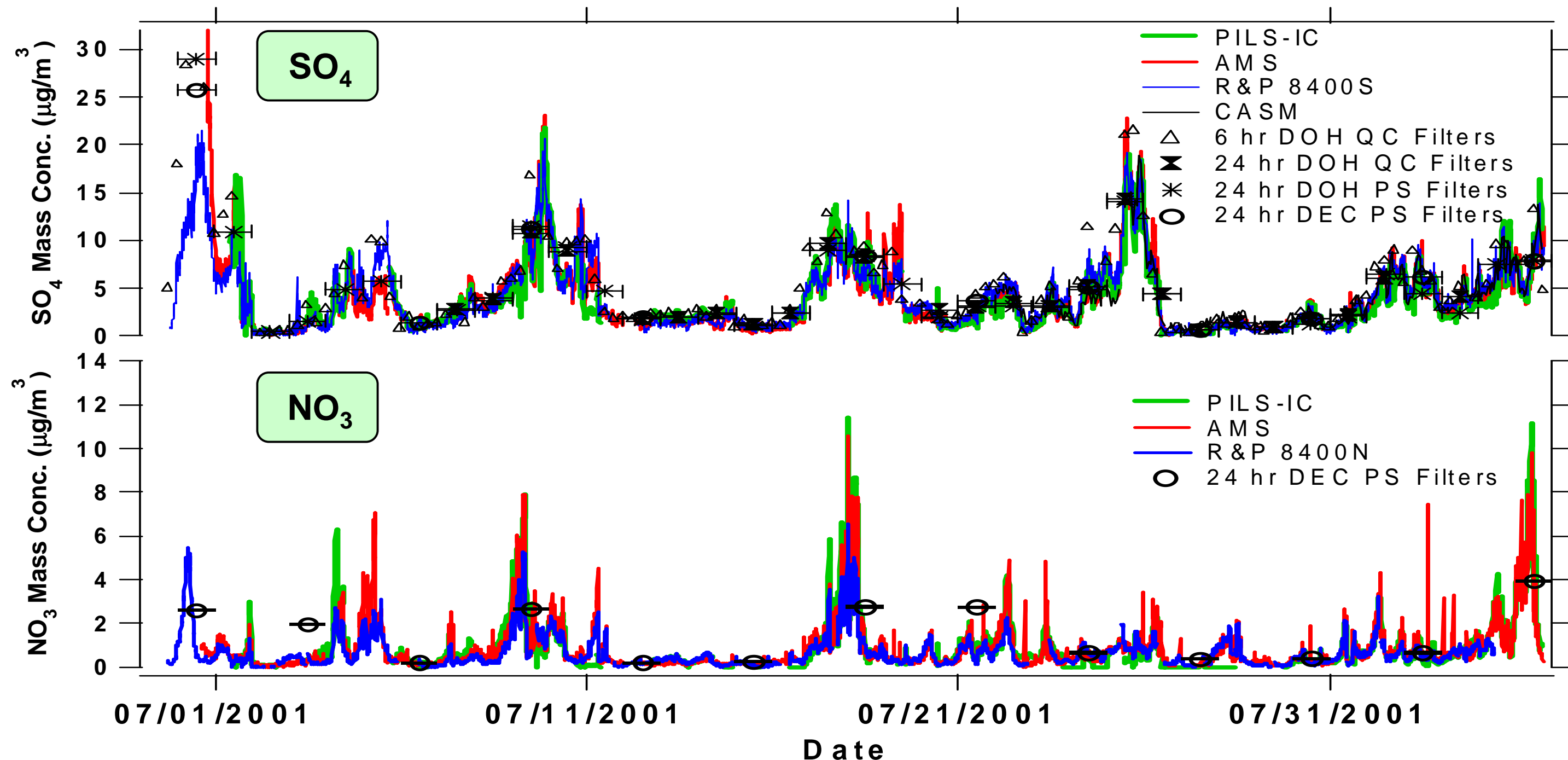


### Site Information:

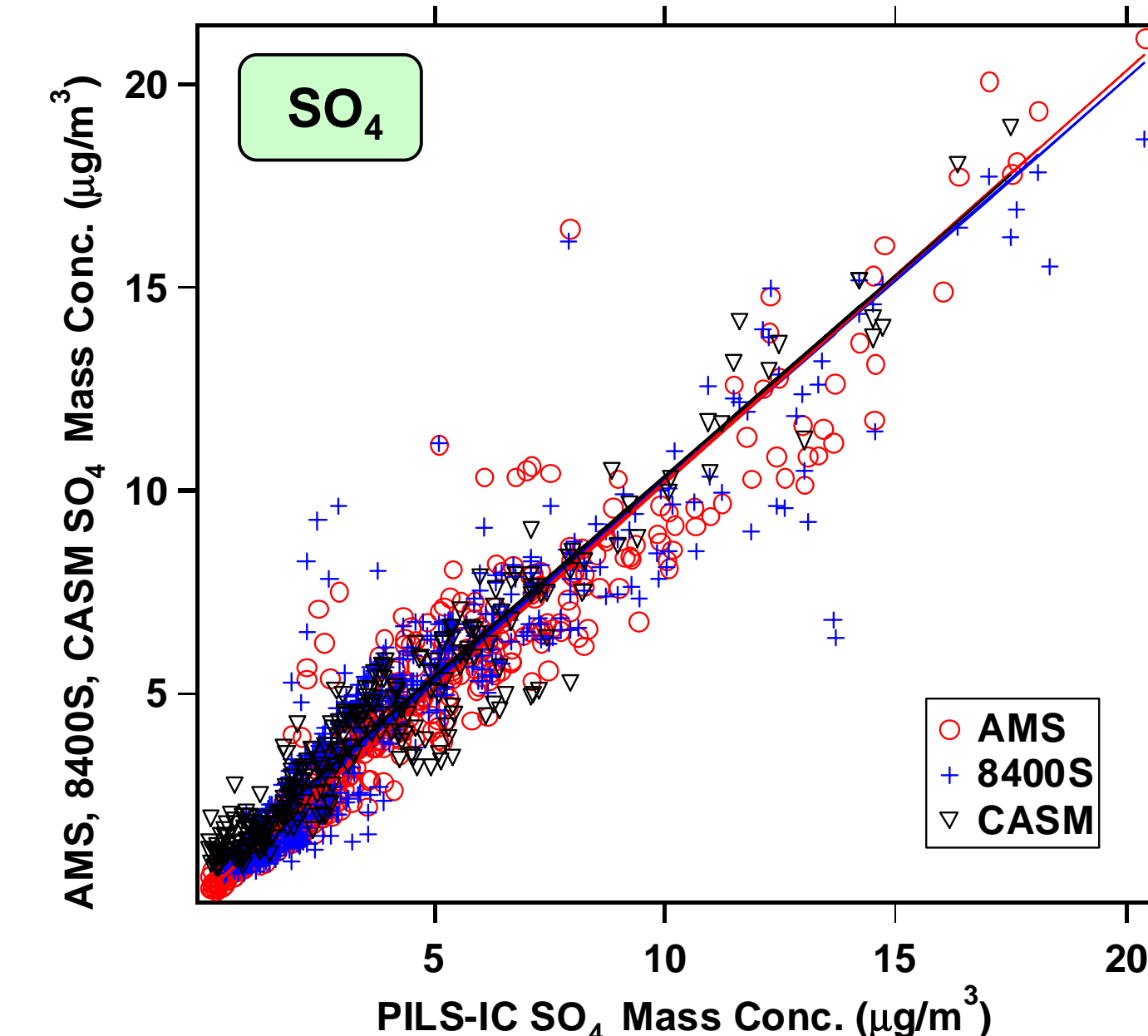
Parking field # 6, Queens College, Queens, New York City (73°49' latitude, 40°44' longitude, ca. 25 m a.S.L.)

- < 1 km south of Long Island Expressway (I-495), ca. 1 km east of Van Wyck Expressway (I-678)

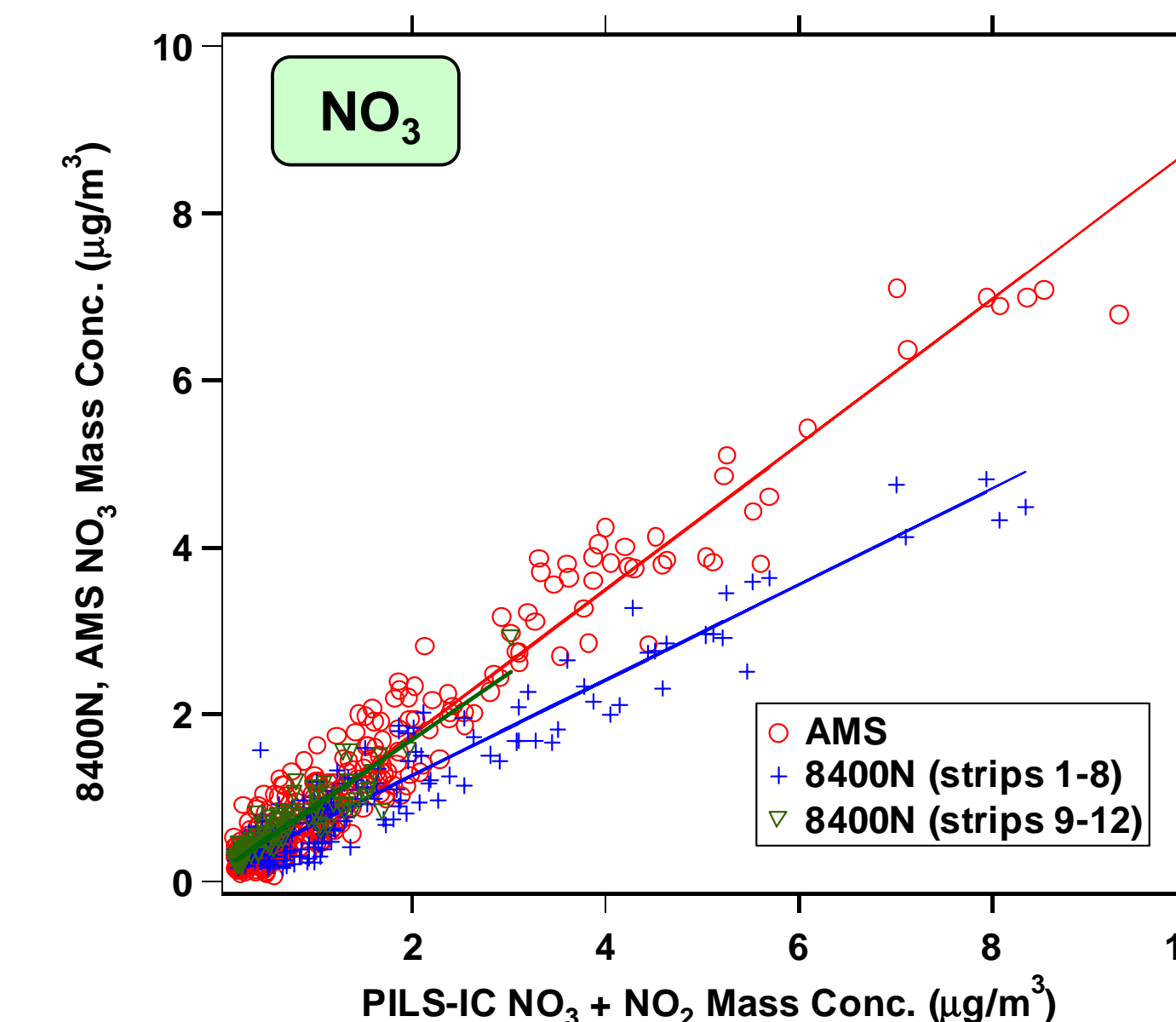
## Mass Concentration Time Series



## Semi-Continuous Instruments Intercomparison



	AMS vs. PILS	8400S vs. PILS	CASM vs. PILS
R <sup>2</sup>	0.91	0.87	0.93
Slope	1.01	0.99	0.99
Intercept, µg/m <sup>3</sup>	0.06	0.36	0.48
Recovery	1.02	1.04	1.06



	AMS vs. PILS	8400N (strips 1-8) vs. PILS	8400N (strips 9-12) vs. PILS
R <sup>2</sup>	0.95	0.91	0.82
Slope	0.87	0.57	0.79
Intercept, µg/m <sup>3</sup>	0.03	0.13	0.12
Recovery	0.88	0.61	0.91

During campaign twelve NiChrome flashing strips were used. Strips 1-8 (used up to July 22<sup>nd</sup>) and 9-12 came from two different batches. Intercomparison results were very different for these two batches.

### Recovery is

- the slope of the linear fit with the intercept constrained to zero;
- used for direct comparison of the magnitude of the instrument responses.

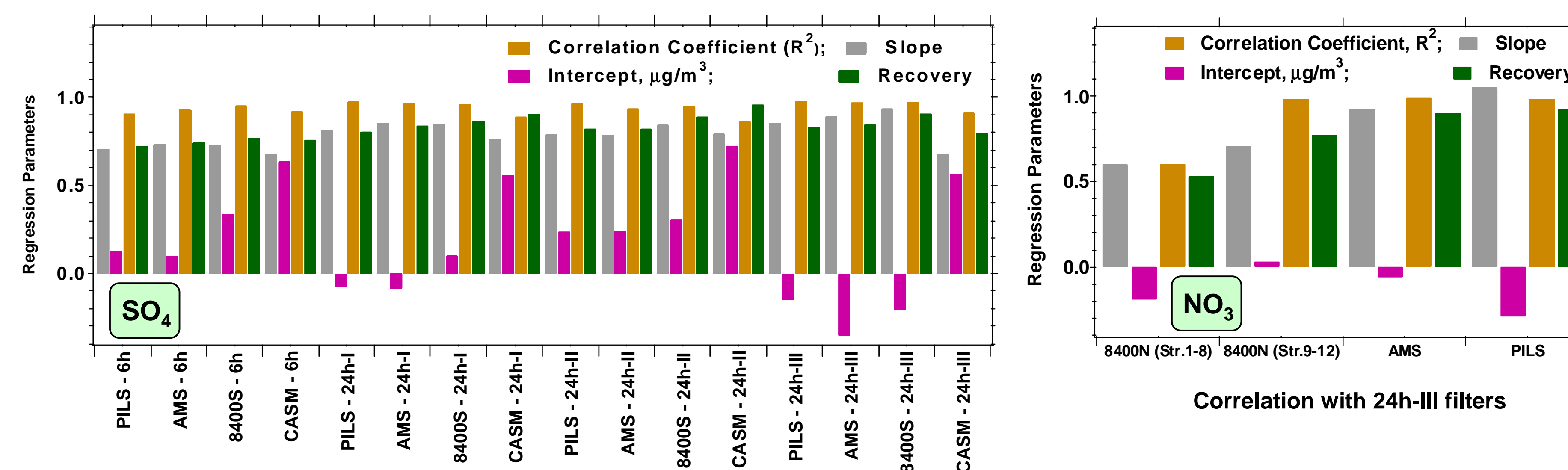
## Comparison of Semi-Continuous Instruments with Filters

### Filter Information

Name	Site	Operator	Sampling Period, Frequency	Data Completeness	Filter Sampler	Inlet Flow, l/min	PM Inlet	Denuder	Analysis
6h	QC	DOH <sup>†</sup>	6/29 – 8/6, 4 per day	98%	Sequential Cyclone Sampler	42	PM3.5 cyclone <sup>§</sup>	No	IC (SO <sub>4</sub> )
24h-I	QC	DOH <sup>†</sup>	7/7 – 8/3, 1 per day	89%	ACCU Sampler	16.7	PM2.5 cyclone	No	IC (SO <sub>4</sub> )
24h-II	PS219 <sup>††</sup>	DOH <sup>†</sup>	6/30 – 8/6, 1 per day	97%	ACCU Sampler	16.7	PM2.5 cyclone	No	IC (SO <sub>4</sub> )
24-III	PS 219 <sup>††</sup>	DEC <sup>‡</sup>	6/30 – 8/5, 1 per 3 days	85%	R&P 2300 Speciation Sampler	10	PM2.5 impactor	Yes (Na <sub>2</sub> CO <sub>3</sub> )	IC (SO <sub>4</sub> , NO <sub>3</sub> )

<sup>†</sup> - Public School 219 is located ca. 100 m west of the Queens College site; <sup>††</sup> - New York State Department of Health; <sup>‡</sup> - New York State Department of Environmental Conservation; <sup>§</sup> - operated at higher flow to get PM2.5

### Results of Linear Regression Analysis



	PILS-IC vs.				AMS vs.				8400S vs.				CASM vs.				PILS vs.	AMS vs.	8400N vs.
	6h	24h-I	24h-II	24h-III	6h	24h-I	24h-II	24h-III	6h	24h-I	24h-II	24h-III	6h	24h-I	24h-II	24h-III	24h-III	24h-III	24h-III
R <sup>2</sup>	0.91	0.98	0.97	0.98	0.93	0.97	0.94	0.97	0.95	0.96	0.95	0.97	0.92	0.89	0.86	0.91	0.98	0.99	0.60* 0.98**
Slope	0.71	0.81	0.79	0.85	0.73	0.85	0.78	0.89	0.73	0.85	0.84	0.94	0.68	0.76	0.79	0.68	1.05	0.92	0.60* 0.70**
Intercept µg/m <sup>3</sup>	0.13	-0.07	0.24	-0.15	0.10	-0.09	0.24	-0.35	0.34	0.10	0.31	-0.21	0.63	0.56	0.73	0.56	-0.29	-0.06	-0.19* 0.03**
Recovery	0.72	0.80	0.82	0.83	0.75	0.84	0.72	0.85	0.77	0.87	0.89	0.91	0.76	0.90	0.96	0.80	0.92	0.90	0.53* 0.77**

### Possible Reasons for Discrepancies Between the Semi-Continuous Instruments and the Filters:

- Over-measurement by filters
  - PM2.5 selector cut-off issues (2 – 5%);
  - Filter artifacts (1 – 2 %)
- Under-measurement by semi-continuous instruments
  - Inlet losses (2 – 5%);
  - Incomplete sampling of PM by semi-continuous instruments (2 - 5%)
  - CASM: SO<sub>4</sub>-to-SO<sub>2</sub> conversion issues (ca. 5%);
  - 8400N: "inadequate" strips 1-8 (NO<sub>3</sub>-to-NO<sub>x</sub> conversion issues?)

## Summary

- Particulate SO<sub>4</sub> was measured by the PILS-IC, the AMS, the R&P 8400S, and the CASM.
- Particulate NO<sub>3</sub> was measured by the PILS-IC, the AMS, the R&P and the 8400N.
- Four sets of SO<sub>4</sub> filter data and one set of NO<sub>3</sub> filter data were collected.
- Almost one-to-one correlation was found between semi-continuous SO<sub>4</sub> instruments.
- Semi-continuous NO<sub>3</sub> instruments agree within 10% (Exception: first three weeks of even lower 8400N measurements; likely explanation: "inadequate" NiChrome strips).
- In most cases, semi-continuous instruments measured 15% less SO<sub>4</sub>, and 10% less NO<sub>3</sub> than filters. Reasons: combination PM2.5 selector cut off issues, inlet losses, incomplete sampling and, possibly, <100% conversion efficiency of some semi-continuous instruments.

## Acknowledgements

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We would like to acknowledge S. Peters from ASRC, U-Albany, D. Diamond and R. Weber from Georgia Institute of Technology for PILS-IC operation and data analysis; and L. Husain and his group from the New York State Department of Health for sulfate filter data. We would also like to thank Queens College for cooperation and logistical support during the campaign.